

PROCESS FOR PREPARING 1,3-DICHLOROACETONE

Background of the Invention

The present invention relates to a process for
5 preparing 1,3-dichloroacetone and epichlorohydrin.

It is known to prepare 1,3-dichloroacetone by the
direct chlorination of acetone with chlorine. See, for
example, U.S. Patent 4,251,467. The process involves the use
of iodine or iodine salts in greater than catalytic amounts.
10 Iodine is very expensive (\$13/kilo according to the 9/23/02
issue of The Chemical Marketing Reporter). For this reason,
it is very important to recover and recycle the iodine or
iodine salts in the process. The extra steps of recovering
and recycling the iodine or iodine salts add significant
15 complexity for building a commercially viable process for a
commodity-type product. Another method for directly
chlorinating acetone involves using methanol instead of
iodine or an iodine salt. However, the major product of this
process is the ketal of the chlorinated species. To get the
20 1,3-dichloroketone, one must hydrolyze the ketal which is not
a trivial process.

It would be desirable to provide a process for
preparing 1,3-dichloroacetone which would eliminate the need
for using iodine and all the associated complexity of
25 recovering and recycling it, as well as eliminate the need
for hydrolyzing the ketal in the case of the latter method.

SUMMARY OF THE INVENTION

In a first aspect, the present invention is a
process for preparing 1,3-dichloroacetone which comprises (1)
30 chlorinating acetone to form monochloroacetone, and (2)
disproportionating the monochloroacetone in the presence of a
platinum catalyst to produce acetone and 1,3-dichloroacetone.

Additionally, a strong acid and, preferably, a chloride source (for example, added as a salt or from hydrolysis of monochloroacetone) and some water may be added to help initiate the reaction.

5 In a second aspect, the present invention is a process for preparing epichlorohydrin which comprises

(1) chlorinating acetone to form monochloroacetone;

(2) disproportionating the monochloroacetone in the presence of a platinum catalyst, optionally, a strong acid
10 and, preferably, a chloride source (for example, added as a salt or from hydrolysis of monochloroacetone) and some water to produce acetone and 1,3-dichloroacetone;

(3) hydrogenating the 1,3-dichloroacetone in the presence of a catalyst to produce 1,3-dichlorohydrin; and

15 (4) cyclizing the 1,3-dichlorohydrin with a base to produce epichlorohydrin.

Other aspects of the present invention will become apparent from the following detailed description and claims.

DETAILED DESCRIPTION OF THE INVENTION

20 The process of the present invention comprises the following steps:

(1) Chlorination

Chlorination of acetone to produce monochloroacetone (MCA) is a well known process. See, for
25 example, U.S. Patent 4,439,623 and U.S. Patent 3,397,240.

(2) Disproportionation

The monochloroacetone produced in step (1) is subjected to a disproportionation reaction to produce both acetone and 1,3-dichloroacetone, in the presence of a
30 platinum catalyst, optionally a strong acid and, preferably, a chloride source (for example, added as a salt or from

hydrolysis of monochloroacetone) and some water. The products may be recovered by known methods, such as extraction or distillation.

Surprisingly, it has been found that heating monochloroacetone with a specific type of catalyst, which is a platinum catalyst, produces acetone and 1,3-dichloroacetone simultaneously, without producing any significant amount of 1,1-dichloroacetone or higher chlorinated by-products.

The platinum catalysts useful in the present invention include any platinum +2 and/or +4 catalysts. Such catalysts are described in U.S. Patent 6,262,280. Examples of suitable catalysts include PtCl_2 and its hydrate, or an alkali metal salt (or its hydrate) of the PtCl_4^{-2} , PtO_2 , chloroplatinic acid, ammonium chloroplatinate, polyamine platinum salts. It is not necessary for the catalysts to be complexed with ligands such as, for example, siloxane complexes.

Preferably, the catalysts employed in the practice of the present invention, are platinum salts. The platinum catalyst is present in a homogeneous form regardless of whether or not it is added as an insoluble salt. If some of the platinum catalyst is leached into the reaction mixture a reaction takes place. If no platinum is leached into the reaction mixture (based on Pt analyses of the liquid phase of the reaction mixture), no reaction takes place. While not wishing to be bound by theory, it is believed that this reaction is related to what goes on in the Shilov-type reaction, described in Luinstra, G.A.; Wang, L.; Stahl, S.S.; Labinger, J.A.; Bercaw, J.E. *J. Organometallic Chem* 1995, 504, 75-91, "C-H activation by aqueous platinum complexes: A mechanistic study."

(3) Hydrogenation

A key feature of the present invention is to hydrogenate the 1,3-dichloroacetone without removing a chlorine atom through the formation of HCl. Such
5 hydrogenation process is described in US Patents 5,744,655, and 6,350,922. The hydrogenation catalysts can be homogeneous or heterogeneous with heterogeneous being most preferred. Use of a heterogeneous catalyst minimizes or
10 eliminates the need to isolate the catalyst for continued use.

The 1,3-dichloroacetone produced in Step (2) is hydrogenated by reaction with a hydrogenating agent to produce 1,3-dichlorohydrin.

15 The hydrogenating agent useful in the present invention may be, for example, molecular hydrogen, an alcohol, or a combination thereof. The hydrogenating agent is preferably molecular hydrogen.

Examples of suitable alcohols useful in the present
20 invention can be primary or secondary alcohols such as methanol, ethanol and C₃-C₁₀ primary and secondary alcohols. Preferably, the alcohol is methanol. Examples of other secondary alcohols useful in the present invention are described in U.S. Patent No. 2,860,146.

25 The maximum quantity of hydrogenating agent source is not critical and is governed by practical considerations such as pressure, reactor efficiency, and safety. When the hydrogenating agent source is gaseous, then the quantity of hydrogenating agent is preferably at least enough to provide
30 the desired pressure. However, in most cases, the reactor preferably contains no more than 1,000 moles of molecular hydrogen per mole of α -chloroketone and more preferably contains no more than 100 moles of molecular hydrogen per

mole of α -chloroketone. Gaseous hydrogenating agent sources, such as molecular hydrogen, are preferably used according to known methods for mixing a gaseous reagent with a liquid reaction mixture, such as bubbling the gas through the mixture with agitation or solubilizing the hydrogen under pressure.

The hydrogenation reaction of the present invention takes place in the presence of a heterogeneous transition metal-containing catalyst.

The transition metal useful as the heterogeneous catalyst of the present invention may be one or more metals selected from any of Groups IB, IIB or IIIA-VIIIA on the periodic table of elements, as currently adopted by the International Union of Pure and Applied Chemistry (IUPAC). The catalyst metal is preferably selected from Group VIIIA of the IUPAC periodic table, including for example, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum and mixtures thereof. The catalyst metal is most preferably platinum.

The temperature of the reaction is not critical, provided that all of the reagents, aside from the hydrogen, remain liquid and in contact with each other. However, low temperatures require longer reaction times and lead to increased levels of impurities. The reaction temperature is preferably at least -10°C , more preferably at least 20°C and most preferably at least 50°C . The reaction temperature is preferably less than 250°C , more preferably no more than 100°C and, most preferably no more than 85°C .

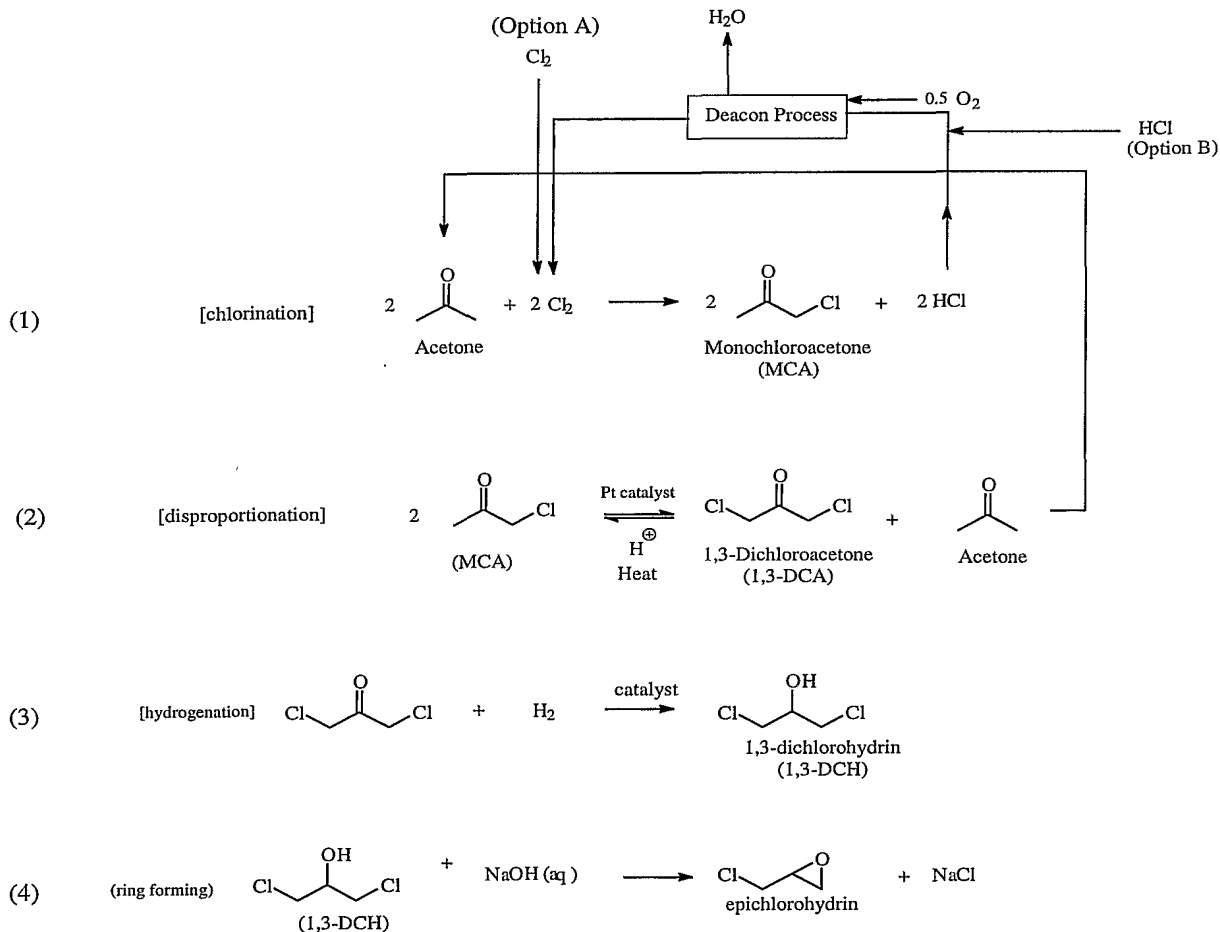
The reaction pressure is not critical as long as there is sufficient hydrogen to run the reaction in the reaction mixture. The pressure is preferably at least 14 psi (97 kPa, 1 atmosphere) and more preferably at least 50 psi (340 kPa, 3.4 atmospheres). The pressure is preferably no

more than 3,000 psi (21 MPa, 220 atmospheres). Higher pressures lead to shorter reaction times.

(4) Ring-Forming or Cyclizing Step

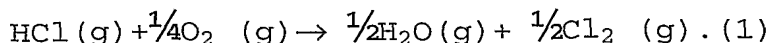
The 1,3-dichlorohydrin produced in step (3) is cyclized to produce epichlorohydrin by contacting it with a strong base, such as an aqueous alkali metal hydroxide, including, for example, sodium hydroxide. This step is well known in the art of manufacturing epihalohydrin. See, for example, U.S. Patent 2,860,146.

The process of the present invention can be represented by the following general equation:



The Deacon Process comprises producing chlorine by direct oxidation of gaseous HCl with O₂ in the presence of a

CuCl₂ catalyst. This process is described by the overall chemical equation:



Reaction (1) in the presence of a CuCl₂ catalyst is
5 a fast overall exothermic process, which is expected to reach equilibrium under normal industrial operating conditions of 700°K to 750°K.

The following working examples are given to
illustrate the invention and should not be construed as
10 limiting its scope. Unless otherwise indicated, all parts and percentages are by weight.

EXAMPLES 1 to 4

GC Conditions

GC: HP 5890 II with FID and 6890 auto-injectors (Front
15 detector)
Column: Rtx-35, Restek Corp., Cat # 10453, ser# 441628
Column type: 35 percent diphenyl - 65 percent dimethyl polysiloxane
Column dimensions: 30m x 0.25 mm x 1.0 um
20 Head pressure: 25 psi
Split vent flow: 50 mL/min
Purge gas flow: 4 mL/min
Air flow: ~300 mL/min
Hydrogen flow: 30 mL/min
25 Make-up flow: 30 mL/min (column flow ~4 mL/min)
Temperature ramp: 55°C for 4 min hold, +15°C/min to 250°C for 10 min.
Run time: 27 minutes
Injector volume: 0.5 uL (5 uL syringe)
30 Injector temp: 200°C
Detector temp: 290°C
Solvent washes: A= acetonitrile, B= 50/50 acetonitrile/water

Integrator: HP ChemStation

The disproportionation reactor was a 4-dram vial equipped with a magnetic stir bar. Monochloroacetone was added to the reactor which contains water, a catalyst as shown in Table I and a strong acid and preferably a chloride salt. The relative amounts of the materials are shown in Tables I-IV. The mixture was stirred and then heated at 95 to 100°C for 17 hours. The product was cooled to room temperature. Ten drops of the filtrate was diluted to 1 mL with acetonitrile, then filtered through a disposable syringe filter and analyzed by gas chromatography. The amounts of products produced are reported by GC area percentages as shown in Tables I to IV (EXAMPLES 1 to 4, respectively).

TABLE I: Results for MCA with Different Non-supported Catalysts
(NOTE: All samples contain MCA and catalyst. Water added to all reaction mixtures.)

Catalyst	Moles cat./Moles MCA	Moles Cl/Moles MCA	Moles H ₂ O/Moles MCA	Area Percent MCA Remaining	Area Percent 1,3-DCA	Area Percent 1,1,3-TCA	Area Percent 1,1-DCA	Area Percent Acetone
HHCP (aq)*	0.0021	0.013	0.57	81	6.4	0.01	2.36	8
PtCl ₂	0.0025	0.0051	0.17	61	11.3	0.06	2.22	10.1
PtO ₂	0.0025	0	0.15	65	11.3	0.05	2.24	9.3
PtCl ₂ / H ₂ Pt(OH) ₆ **	0.0026	0.0046	0.06	59	10.0	0.05	2.34	7.96
Pt powder	0.0030	0.0093	0.15	94	0.27	0.00	2.03	1.71
CoCl ₂	0.0027	0.0054	0.15	94	0.27	0.01	2.06	1.77
CuCl ₂	0.0026	0.0051	0.16	92	0.28	0.00	2.05	1.77
CuCl ₂ (repeat)	0.0026	0.0053	0.14	95	0.28	0.00	2.05	1.06
CuCl	0.0027	0.0055	0.16	94	0.28	0.00	1.97	1.69
FeCl ₃	0.0024	0.0047	0.16	94	0.27	0.01	2.03	1.99
HgCl ₂	0.0024	0.0047	0.15	94	0.27	0.01	2.03	1.94
IrCl ₃	0.0024	0.0047	0.14	95	0.26	0.00	2.01	0.50
IrCl ₄	0.0025	0.0050	0.14	94	0.26	0.01	2.05	1.76
PdCl ₂	0.0024	0.0047	0.17	94	0.27	0.01	2.03	1.93
RuCl ₂	0.0023	0.0047	0.14	95	0.26	0.00	1.85	1.73
RhCl ₂	0.0022	0.0045	0.17	94	0.27	0.02	2.03	1.67
TiCl ₃	0.0029	0.0057	0.15	94	0.27	0.01	2.03	1.83
TiCl	0.0026	0.0052	0.16	95	0.26	0.00	2.02	0.72
ZrCl ₄	0.0030	0.0061	0.13	71	0.35	0	3.09	2.62
MCA only	NA	NA	NA	95	0.17	0.00	2.28	0

*HHCP = hydrogen hexachloroplatinate (IV), 8 wt percent solution in water. Formula weight H₂PtCl₆ = 409.82.

**The PtCl₂ contributed ~46 percent of the moles of Pt.

- A source of a strong acid is preferred at the beginning of the reaction. It helps to accelerate the reaction.

The data in Table I show that only the Pt(+2) and Pt(+4) catalysts produced significant amounts of 1,3-dichloroacetone without producing any significant amounts of 1,1-dichloroacetone or higher chlorinated by-products.

5 TABLE II: Results for MCA with PtO₂ (with and without HCl) vs Time

(NOTE: All samples contain MCA (2g). 5 wt percent HCl was used with PtO₂ and 11 wt percent HCl was used with Pt/carbon)

	Time (hours)	Moles Pt / Moles MCA	Moles Cl / Moles MCA	Moles H ₂ O / Moles MCA	Area Percent MCA Remaining	Area Percent 1,3-DCA	Area Percent 1,1,3-TCA	Area Percent 1,1-DCA
PtO ₂ (no HCl)	6.5	0.0027	0	0.15	92	1.0	0.01	2.05
PtO ₂ (with HCl)	6.5	0.0027	0.0076	0.29	79	7.8	0.02	2.07
PtO ₂ (no HCl)	~22.5	-	0	-	60	11.2	0.05	2.31
PtO ₂ (with HCl)	~22.5	-	0.0076	-	65	11.3	0.05	2.24
MCA only	NA	NA	NA	NA	95	0.17	0	2.28

10 The data in Table II indicate that adding HCl to the reaction mixture in the presence of a platinum catalyst early in the reaction (6.5 hours after start of reaction) helps get the reaction started sooner.

15 TABLE III: Results for MCA with Different Acids

(NOTE: All samples contain MCA (2g), 5 wt percent Pt on carbon (0.2 g), acid and water)

Acid	Moles Pt / Moles MCA	Moles Cl / Moles MCA	Moles H ₂ O / Moles MCA	Area Percent MCA Remaining	Area Percent 1,3-DCA	Area Percent 1,1,3-TCA	Area Percent 1,1-DCA
HCl	0.0023	0.029	0.468	73	10	0.04	2.32
H ₂ SO ₄	0.0026	0	0.549	90	2	0.02	1.99
p-TSA hydrate*	0.0025	0	0.457	80	3	0.01	2.37
MCA only	NA	NA	NA	95	0.17	0	2.28

*p-TSA = para-toluenesulfonic acid dihydrate

20 The data in Table III indicate that HCl performs better than the other strong acids for running the disproportionation reaction.

TABLE IV: Results for MCA with 5 wt percent Pt on carbon catalyst and LiCl

(NOTE: All samples contain MCA (2g) and 5 wt percent Pt on carbon (0.2g))

	Moles p-TSA* / Moles MCA	Moles Cl / Moles MCA	Moles H ₂ O / Moles MCA	Area Percent MCA Remaining	Area Percent 1,3-DCA	Area Percent 1,1,3- TCA	Area Percent 1,1- DCA
MCA only	NA	NA	NA	95	0.17	0.00	2.28
LiCl (dry)	0	0.228	0	85	5	0.03	2.15
LiCl + Water	0	0.156	0.450	84	6	0.02	2.11
LiCl + p-TSA	0.051	0.255	0.102	63	15	0.11	2.28
p-TSA only	0.052	0	0.104	63	0.22	0.02	3.18

*p-TSA = para-toluenesulfonic acid dihydrate

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The data in Table IV indicate that a chloride salt helps generate the disproportionation reaction.